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(54) Production of 1-butene

(57) 1-Butene is produced from a C_4 hydrocarbon charge comprising n-butane, 1-butene, 2-butene, isobutene and a diolefinic and/or acetylenic hydrocarbon by first converting the isobutene of the charge, by reaction with a saturated C_{1-4} aliphatic alcohol, essentially to an ether; separating the ether and the residual alcohol from the residual C_4 cut and thereafter subjecting the latter to a selective hydrogenation of the acetylenic or diolefinic hydrocarbons and, after separation of hydrogen from the resulting product, distilling the latter and extracting by means of a solvent the 1-butene contained in the distillation top fraction.

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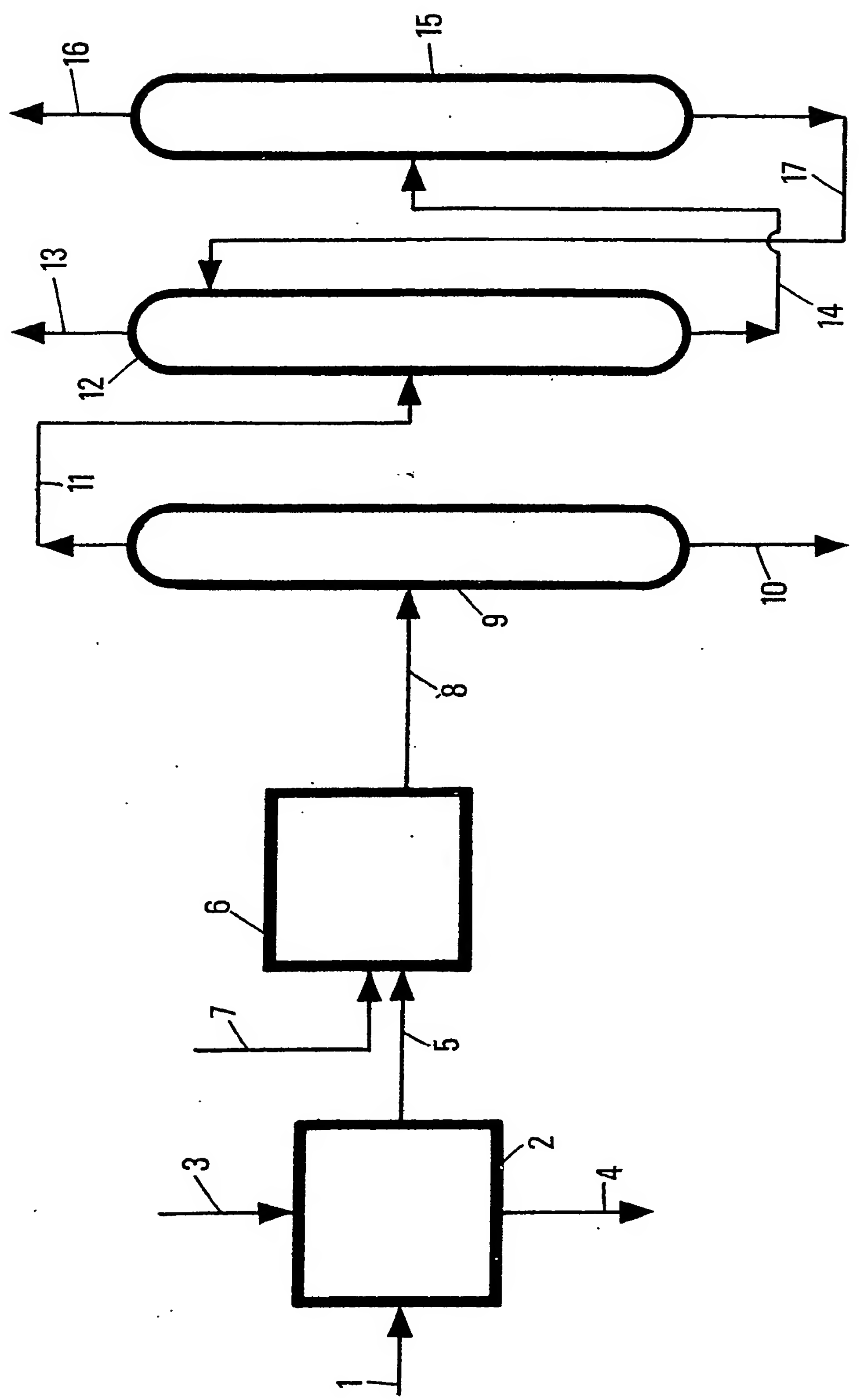
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SPECIFICATION
Production of l-butene

This invention concerns a process for producing l-butene from a C_4 hydrocarbon cut.

Among the C_4 mono-olefins, 1-butene is of particular interest. It can be polymerized to poly-l-butene, which is one of those rare polymers that exhibit a good resistance to high temperatures and may thus be used in the manufacture of hot water pipes used in the building industry. l-butene is also used as co-monomer in certain ethylene polymerization processes for the production either of high-density polyethylene or of low-density polyethylene at low pressure.

Hitherto, however, it has not been possible to develop the market for l-butene to a large scale in view of its high price, and the present invention is based on the discovery of a more efficient process for manufacturing l-butene that makes possible the production of this compound at a really competitive price.

In accordance with the present invention, a C_4 hydrocarbon cut comprising at least n-butane, l-butene, 2-butene, isobutene and at least one diolefinic or acetylenic hydrocarbon is subjected to the following operations:

(a) reaction with at least one saturated aliphatic alcohol having from 1 to 4 carbon atoms, in the presence of an acid catalyst, so as to remove at least 95% of the isobutene by converting the latter to an ether, and separation of said ether and of the unconverted alcohol from the C_4 cut,

(b) reaction of the C_4 cut from step (a) with hydrogen, in the presence of a hydrogenation catalyst, under hydrogenation conditions that are selective for the acetylenic and/or diolefinic hydrocarbons (i.e. a hydrogenation that is as limited as possible with respect to the *n*-olefins) and with as low an isomerization of l-butene as possible (i.e. with a conversion of l-butene lower than 15% and preferably, lower than 5%),

(c) distillation of the product from step (b) under conditions essentially providing a bottom fraction comprising at least 96% (preferably at least 99%) of 2-butene and at least the major part of *n*-butane and a top fraction comprising at least the major part of 1-butene together with isobutane, when present, and a minor proportion of *n*-butane, and

(d) treatment of the top fraction from step (c) in an extraction zone, preferably by extractive distillation, so as to recover, at the bottom, the desired l-butene and, at the top, the saturated hydrocarbon (isobutane and possibly *n*-butane).

Preferably, in step (c), at least 96% (and more advantageously at least 99%) of the 2-butene and less than 20% of the l-butene is recovered at the bottom and, preferably, at least 80% of the l-butene and less than 4% (advantageously less than 1%) of the 2-butene is recovered at the top.

The C_4 hydrocarbons cuts which are of particular interest according to the invention are those obtained by hydrocarbon conversion producing olefins, followed by extraction of at least the major part of the 1,3-butadiene produced. These cuts contain at least one C_4 saturated hydrocarbon (*n*-butane and possibly isobutane), monolefinic hydrocarbons (1-butene, 2-butene and isobutene) and at least one diolefinic hydrocarbon (particularly 1,3-butadiene) and/or acetylenic hydrocarbon (propyne, ethylacetylene and/or vinylacetylene).

By way of example, an unsaturated C_4 cut, after conventional extraction of butadiene, contains, by weight:

saturated hydrocarbons (butane or isobutane):	—1—15D%
isobutene:	20—70%
1-butene:	10—40%
2-butene:	5—30%
Diolefinic and acetylenic hydrocarbons:	0.1—5%

This cut constitutes a charge which may be treated according to the process of the invention. Small amounts of C_3 and C_{5+} hydrocarbons may also be present.

The technique of preliminary removal of 1,3—butadiene is of no importance for the present process. In some case at least a portion of the acetylenic hydrocarbons and of the other diolefins may be simultaneously extracted.

Isobutene from the C_4 cut is first reacted with an alcohol, in the presence of an acid catalyst, for example, sulfuric acid, hydrofluoric acid, aluminum chloride or boron fluoride. It is however preferred to make use of carbonaceous substances containing SO_3H groups, for example sulfonated coals, for example Nalcite X or AX, Zeo-Karb-H, (Registered Trade Mark), sulfonated phenol-formaldehyde resins (for example Amberlite Registered Trade Mark) IR—100, Nalcite MX), sulfonated coumarone indene polymers or, preferably, sulfonated polystyrene divinylbenzene resins, for example Dowex (Registered Trade Mark) 50, Nalcite HCR and Amberlyst (Registered Trade Mark) 15.

When operating continuously, the volume of the treated charge per volume of catalyst and per hour is generally from 0.5 to 20. Usually the operating temperature is 20—150°C, preferably 40—100°C, with from 0.9 to 10, preferably from 1 to 2 moles of alcohol per mole of isobutene, an alcohol excess favouring the reaction.

The alcohol may be, for example, ethanol or preferably methanol.

The etherification reaction is well known and described, for example, in US patents No. 2 480 940, No. 3 037 052 and No. 3 281 475.

It is clear that 1-butene will be the easier to purify as the conversion rate of isobutene, in the first step, is higher. Accordingly, the conditions will be so selected as to obtain a conversion rate of at least 95%, preferably at least 99% of isobutene. These conditions are fulfilled, for example, by the process according to the French patent application No. 7 910 399, filed on April 24, 1979.

At the end of this first step, the formed ether and the residual alcohol are separated from the unreacted C_4 hydrocarbons. This separation may be achieved according to any known technique, for example by adsorption, water washing, distillation or a combination thereof. The distillation has some disadvantages due to the formation of azeotropes; numerous proposals have been made for obviating this disadvantage; this point will not be discussed here.

The hydrocarbon cut, whose isobutene content has been decreased, after removal of the ether and the residual alcohol is subjected, in step (b) to a non-isomerizing selective hydrogenation.

The selective hydrogenation of the acetylenic and diolefinic hydrocarbons in the presence of mono-olefins is performed in the presence of a noble metal catalyst. A preferred catalyst is palladium.

The catalyst may be supported on such carriers as, for example, alumina, silica, a spinel or coal. A preferred catalyst comprises 0.01—2% by weight of palladium on alumina.

The hydrogenation temperature depends on the catalyst; in most cases it ranges from 10 to 100°C, preferably from 0 to 40°C.

The operation is conducted in the vapor phase or, preferably, in the liquid phase, in the presence of hydrogen, and the pressure may be, for example, from 1 to 30 atmospheres, preferably 1—10 atmospheres. The hydrocarbon flow rate is, for example, from 1 to 50 (liquid) volumes per volume of catalyst and per hour. For example, 1 to 2 moles of hydrogen are used per mole of acetylenic or diolefinic hydrocarbon.

After separation of the hydrogenating gas, the hydrocarbon cut is subjected to a fractionation by distillation (step c). This is performed preferably by the deep fractionation technique (superfractionation), with one or more columns comprising a total of, for example, 40 to 250 theoretical plates. The severity of the fractionation depends on the desired purity for 1-butene and 2-butene.

At the end of step (c), the hydrocarbons mixture obtained as top product (essentially 1-butene and at least one saturated hydrocarbon) is subjected to a liquid-liquid extraction or preferably to an extractive distillation of conventional type.

As extraction polar solvent, there can be used, for example, dimethylacetamide, dimethylformamide, furfural, N-methyl pyrrolidone, formylmorpholine or acetonitrile. Many other solvents are known and the invention is not limited to the selection of specific solvents. It is however preferred to make use of dimethylacetamide.

From the top are recovered the saturated hydrocarbons and from the bottom a solution of 1-butene in the extraction solvent. The 1-butene may be removed by mere distillation, by stripping or by re-extraction making use of a non-miscible auxiliary solvent such as a paraffinic hydrocarbon easily separable, by distillation, from the 1-butene.

The invention is illustrated by the accompanying drawing. The C_4 hydrocarbon charge issued from a butadiene extraction unit, is supplied through line 1 to the reaction zone 2 fed with alcohol through line 3. After fractionation of the products, the formed ether is recovered from line 4 and the residual hydrocarbons from line 5. The latter, previously cleared from the residual alcohol by a convenient treatment, for example by washing with water, are treated with hydrogen, introduced through line 7, in the hydrogenation zone 6.

After separation of the residual hydrogenating gas, the hydrocarbons are fed through line 8 to the distillation zone 9. At the bottom thereof, there is recovered nearly all 2-butene (at least 96%, preferably at least 99%) and the major portion of n-butane through line 10. The top product (at least 50% of 1-butene subjected to distillation, preferably at least 90%, as well as isobutane and traces of other hydrocarbons, if any) is fed through line 11 to the extractive distillation zone 12. The paraffins are separated at the top and a solution of 1-butene in the extraction solvent at the bottom (line 14). This solution is re-distilled in column 15. 1-butene is recovered through line 16 and the extraction solvent is fed back through line 17 to zone 12.

EXAMPLE:

The treated hydrocarbon C_4 cut has been obtained by steam-cracking and was subjected to a butadiene extraction. After this extraction, its composition (% by weight) is that given in Table I, column A.

This cut, with additional methanol, is passed over a catalyst formed of a sulfonated ion-exchange resin based on polystyrene cross-linked through divinylbenzene (Amberlyst 15). The temperature was

50—90°C and the pressure 10—20 bars. The molar ratio methanol/isobutene was 1.14. The operation was conducted according to the technique described in the French patent application No. 7 910 399 (Example 2), comprising two reaction stages with the intermediate separation of MTBE, washing of the C_4 cut with water and recycling of the unconverted methanol.

The total conversion of isobutene was 99.8% and the obtained C_4 cut had the composition reported in Table I, column B.

The C_4 cut, substantially cleared from isobutene (content lower than 0.2% by weight) was subjected, in the presence of additional hydrogen, to a selective hydrogenation under the following conditions:

Catalyst: 0.3% by weight of palladium on alumina

Conditions: temperature: 5°C; pressure: 3 kg/cm²; hydrocarbon liquid charge hourly flow rate: 10.

The hydrogen amount corresponds to 1.2 times the theoretical amount required for hydrogenating butadiene to butene.

The composition of the effluent is reported in Table I, column C.

After separation of the unconverted hydrogen, the hydrogenated C_4 cut (whose butadiene content was lower than 10 ppm by weight) was fed to a distillation unit comprising two serially connected columns, each of 70 plates, with a reflux rate of 14 with respect to the distillate.

At the bottom of the second column, 2-butene was recovered with almost all of the n-butane.

At the top almost all the isobutane and the major portion of 1-butene was recovered. The molar compositions of the top and bottom effluents are given in Table I (columns D and E).

The top effluent of said distillation forms the feed charge of an extractive distillation column with 60 plates. The solvent, consisting of dimethylformamide, is fed to the column at the 8th stage from the top, at a flow rate of 4.2 times that of the feed charge. The top vapors are condensed; one half of the condensate is recycled to the top of the column, as reflux, while the other half of the condensate is discharged from the system.

The residue, essentially formed of dimethylformamide and 1-butene, is fed to the solvent regeneration column comprising 40 plates. The bottom effluent from said column constitutes the regenerated dimethylformamide and is recycled to the extractive distillation column as above defined.

The top effluent is purified n-butene whose composition is given in column F of Table I.

TABLE I

Composition (% b.w.)	Charge (A)	Outflow Step (a) (B)	Outflow Step (b) (C)	Distillation Top Effluent (D)	Distillation Bottom Effluent (E)	1-Butene (F)
C_3 hydrocarbons	0.3	0.6	0.6	1.27		
Isobutane	1.2	2.2	2.2	4.66		0.06
n-butane	5.8	11.0	12.0	1.06	21.77	0.32
isobutene	47.3	0.2	0.2	0.41	0.02	0.44
1-butene	27.0	51.0	48.5	92.53	9.18	99.10
2-butene	18.0	34.2	36.1	0.07	68.27	0.08
Butadiene	0.2	0.4	10 ppm			
C_5 hydrocarbons	0.2	0.4	0.4		0.76	

CLAIMS

1. A process for producing 1-butene form a C_4 hydrocarbon cut comprising at least n-butane, 1-butene, 2-butene, isobutene and at least one diolefinic or acetylenic hydrocarbon, comprising the steps of:

1)—reacting said C_4 hydrocarbon cut with at least one saturated aliphatic alcohol having from 1 to 4 carbon atoms per molecule, under such conditions as to convert at least 95% of the isobutene, essentially to an ether, and separating thereafter the residual C_4 cut from said ether and from the uncoverted alcohol,

2)—reacting said residual C_4 cut from step (1) with hydrogen, in contact with a hydrogenation catalyst, under conditions of both selective hydrogenation of the acetylenic or diolefinic hydrocarbons and limited isomerization of 1-butene to 2-butene, and separating thereafter the hydrocarbon product from the unconverted hydrogen,

3)—distilling the hydrocarbon product from step (2) under such conditions as to obtain, as bottom fraction, at least 96% of the 2-butene and at least the major portion of the n-butane and, as top fraction, at least the major portion of the 1-butene with isobutane, when present, and the n-butane which has not been recovered in the bottom fraction, and

4)—treating the top product from step (3) with a solvent in an extraction zone to provide a raffinate and an extract, and fractionating the extract to separate the 1-butene from the solvent.

2. A process according to claim 1, wherein step (2) is performed with a palladium catalyst at a temperature from —10 to 100°C and under a pressure of from 1 to 30 atmospheres.

3. A process according to claim 1 or 2, wherein step (3) is performed in a distillation zone of an efficiency equivalent to 40—250 theoretical plates.

4. A process according to one of claims 1 to 3, wherein step (3) is performed by withdrawing at least 99% of the 2-butene from the bottom and at least 90% of the 1-butene from the top.

5. A process according to one of claims 1 to 4, wherein step (4) is performed by extractive distillation with dimethylformamide.

6. A process according to one of claims 1 to 5, wherein the C_4 hydrocarbon cut contains at least the following hydrocarbons, in the following proportions by weight:

saturated hydrocarbons (butane and isobutane, if any):—	1—15%
isobutene:—	20—70%
1-butene:—	10—40%
2 butene:—	5—30%
diolefinic and/or acetylenic hydrocarbons:—	0.1—5%

7. A process according to claim 2, wherein the temperature is from 0 to 40°C and the pressure from 1 to 10 atmospheres.

8. A process according to claim 7, wherein the hydrogen amount is 1 to 2 moles per mole of acethylenic or diolefinic hydrocarbon.

9. A process according to one of claims 1 to 8, wherein the conditions of the reaction with a saturated aliphatic alcohol are such as to convert at least 99% of the isobutene.

10. A process according to Claim 1 carried out in apparatus as diagrammatically illustrated in the single figure of the accompanying drawings.

11. 1-Butene obtained by a process as claimed in any one of the preceding claims.

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